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Hybrid nylon-6/silica nanocomposites with improved mechanical properties

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ABSTRACT

The study involves the development of new strategies to form technically interesting hybrid nanocomposites with improved mechanical properties. In particular, a new 'dissolution' preparative route was developed which incorporates silica nanoparticles (<30 nm) into a nylon-6 matrix. The procedure relies on the judicious choice of organic solvent and pH control. The synthesis involves the dissolution of nylon-6 in formic acid followed by silica particle addition (as an acidified, monodisperse sol) with stirring. Viscous solutions were prepared under cleanroom conditions and casted as thin films which are dried and vacuum treated at ~60°C. TEM images revealed that the silica particles i.) retained their original shape and size (10-30 nm), ii.) are mono-dispersed and iii.) mainly non-agglomerated. The degree of crystallinity of the composites was determined with XRD as a function of percentage filler added. The nylon-6 phase is semi-crystalline while the silica phase is amorphous. Initial mechanical tests on the composites were conducted and showed with 1wt% silica addition, the E modulus was increased to ~2600 MPa. The increase in mechanical properties may be a result of the nanosize filler particles which has good synergy with the nylon matrix. Friction and wear properties were also investigated on a pin on disk tribometer by running a flat pin of steel against the composite disc.

INTRODUCTION

During the past decades Polyamide-6 (PA-6) has occupied a prominent place in engineering thermoplastics due to its wide spectrum of properties [1]. The mechanical properties of PA can be modified by the addition of inorganic fillers as low cost reinforcement material [2]. Fillers widely used are calcium carbonate, talc, silica and glass fiber, which play an important role in the plastics filler market [3]. The influence of these fillers on the polyamide depend strongly on their shape, particle size, distribution and surface characteristics [4]. A composite with improved properties and a low particle concentration (to preserve the good properties of pure PA) is desired. Since silica (SiO₂) is very versatile [5] and can be modified as required (different particle size, pH, morphology etc.) it is one of the most applied fillers in thermoplastic polymer composites and has been applied for automotive applications, electric engineering, electronics, appliances and consumer goods [6].

It has been established that the filler particle size and degree of dispersion have a pronounced influence on the composite properties. Increased aggregation of fillers with decreasing particle size is a commonly observed adverse effect and control of the dispersion through appropriate processing conditions remains as a major challenge [7].

The aim of the present investigation was to a) seek a general and facile room temperature synthesis strategy by which nanoscale inorganic filler particles can be well dispersed into a

polyamide matrix, b) determine stress-strain relationships and c) friction behavior. The motivation to obtain good dispersion stemmed from the observation that if any properties are to be further improved, then the distribution of the inorganic filler particles in the polymer matrix has to be as homogeneous as possible. Our procedure was based on selecting appropriate reaction conditions, particularly with regard to solvent choice and pH control. The silica dispersion remained stable due to sufficient proton adsorption that maintained a (positively) charged surface in solution. Solvent use was kept to a minimum to ensure concentrated, highly viscous solutions could be cast on clean glass surfaces followed by a combination of vacuum and heat (60-80°C) treatments to remove the solvent.

Another important application of nylon-6 is seen in the rapid growth in the use of thermoplastic as wear resistant materials to substitute metals [8]. Dry polymer-metal sliding bearings are frequently used because of the advantages for example regarding cost and easy assembly in production. By using nanoparticles (high surface area) it is expected to have even better adhesion between polymer and matrix. In addition, factors that exert influence on friction and wear characteristics of the polymer composites are also the particle size of the filler. If the particles are large and hard, they can be easily removed out of the matrix material and contribute to the wear of composites by their abrasive action and cause wear and damage of counterpart material [9]. The easy fall-out of large hard particles under tribological conditions is then avoided.

Silica nanoparticles are currently used for the enhancement of the mechanical properties in polyamide-6 [10]. In this study, the effect of the addition of nano-silica on the tribological performance and on the materials microstructure of the PA-6 was investigated as well.

EXPERIMENTAL DETAILS

Commercial polyamide-6 was used (Aldrich). The inorganic filler used was silica sol (SNOWTEX). The preparation of the polymer solution has been described elsewhere [11]. Nylon films were produced by drawing a steel knife over a pre-treated glass containing a solution of the polymer in formic acid at a rate of 1 mm min⁻¹ using Dr Blade™ equipment. A surface treated glass with ethanol and acetone was used for a better adhesion of the polymer solution to the glass. Film thickness varied slightly due to the presence of a semicrystalline spherulitic microstructure. The composite was left overnight and a film-coating of 0.1 to 0.5 mm was formed on the glass.

Mechanical testing: All samples were prepared with compression moulding. The polymer nanocomposite was melted and given a certain shape by compression of the melt. The samples were dried in a vacuum oven at 80°C for 2 days. Plates of 1 mm thickness were moulded and the test samples were machined out of the plates. The elastic modulus was measured at a tensile speed of 1 mm/min and the displacement was measured with an extensometer with a gauge length of 10 mm. Yield stress, strain-at-yield and strain-at-break were recorded on a Zwick Z010 apparatus.

Tribological measurements: Before tribological measurements the film casted nanocomposites were compression moulded into sheets of about 19x5.5x1 mm at 250-260°C. Compression was performed in 3 steps: 2 min at 5 MPa and , 3 min at 10 MPa and 5 min at 20MPa at 250°C. The samples were cooled at room temperature. The investigated polymers were cut into discs with diameter of ca. 40 mm and a thickness variation between 0.9 and 1.07 mm. The discs surface

roughness varies from $R_a=0.5$ to $1.4\text{ }\mu\text{m}$. The roughness of the pin was $R_a = 0.15\text{ }\mu\text{m}$. Dry sliding wear tests samples were performed with a pin-on-disc tribometer (CSEM, Neuchatel, Switzerland), placed in a climate chamber (Heraeus, HC4057, Balingen, Germany) at 23°C and 40% relative humidity. The test set-up consisted of a flat round steel pin 100McCrW4 sliding against a rotating polymer sample. The sliding velocity for the nanocomposites was set at 0.1 m/s to avoid the occurrence of a high PV value for nylon and of possible thermally induced fracture processes. The load used was 1 N and the mean initial contact pressure was 0.7 MPa with a pin of 1.3 mm . The resulting PV was then $75339\text{ N/m}\cdot\text{s}$. The sliding distance of the tests was adapted for each specific measurement to obtain significant wear and to detect possible fatigue. Measurements for nano - composites were set at 10 km of sliding distance. The coefficient of friction was measured on-line by monitoring the ratio between the measured shear force and the applied normal force through measurement of the deflection of the pin-arm (lever) with two inductors. Wear measurements by weight lost of the samples were initially performed but preliminary results indicated that the moisture had a negative influence in the experiments with a varied weight from the sample over time. The wear track depth was measured with a micromap 512 Opto-profiler.

Instrumentation: Transmission Electron Microscopy (TEM) micrographs were obtained using a JEOL 2010F equipped with a field-emission gun operating at 200 kV . TEM samples were prepared by ultramicrotoming thin sections of the polyamide/silica nanocomposite with a diamond knife. These thin sections were then captured on Formvar coated Ni grids. The particles observed in the micrographs were unambiguously identified as silica by using both X-Ray Energy Dispersive Spectrometry (EDAX R-TEM Sapphire detector equipped with a super-ultra thin window) and Energy Filtering (Gatan Imaging Filter 2001) attached to the TEM. Powder XRD data were collected on a Philips X'Pert-1 PW3710 diffractometer using $\text{Cu-K}\alpha$ ($\lambda=1.542\text{ \AA}$) radiation with a secondary curved graphite monochromator. XRD data verified the amorphous state of the silica particles (no peaks observed) while the nylon-6 was semi-crystalline. Quantitative XRF was used to determine the amount (as wt.-%) silica present in each bulk sample. Analysis was performed on a Philips PW 1480/10 fluorometer (Eindhoven, The Netherlands). The calculation method used the program FPMulti that has been previously described [12].

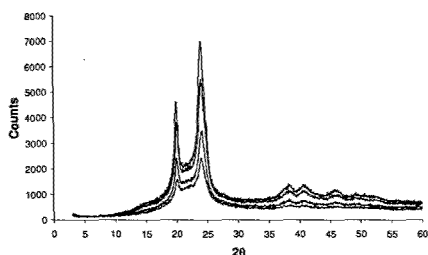


Figure 1. X-Ray diffraction of nylon-6 nanocomposites

RESULTS AND DISCUSSION

Dispersion and mechanical tests

The crystallinity of the formed composites was followed with X-Ray diffraction (XRD) as a function of percentage filler added. The XRD data of a composite containing variable amounts of silica filler percentage is shown in Figure 1. It was observed that the nylon-6 component was semi-crystalline while the silica phase was, with no discernable peaks, amorphous.

For the TEM investigation the sample was microtomed to a thickness (~80 nm) where the silica particles showed good visual contrast with the polymer matrix. Two TEM pictures taken from different sample localities revealed an even distribution of the silica particles throughout the matrix. The TEM micrographs clearly indicated several unique properties of the composite resulting from the improved synthesis method, namely a) silica particles were all in the 10-30 nm size range, b) silica particles were non-agglomerated and c) silica particles were well dispersed (good homogeneity) inside the polyamide matrix. Scheme 1 shows the TEM pictures of a 3wt% sample. We chose filler additions in the range 1-5 mol% because it was evident from current methods that a maximum of 5 mol% filler loadings already leads to optimum mechanical properties [2].

The main difficulty of this technique lies in removing the solvent from the films. This is avoided by treatment of the films in a very high vacuum oven 10^{-7} Mbar. SEM

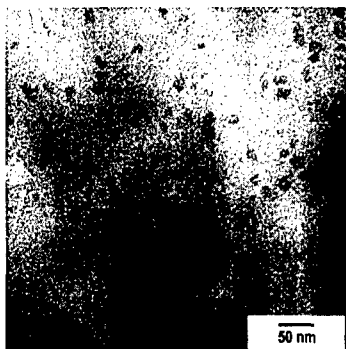


Figure 2. Silica homogeneously dispersed

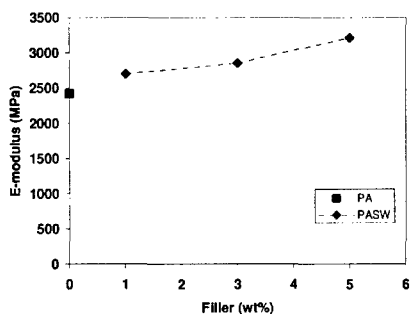


Figure 3. Variation in the elastic modulus for composites with different filler percentages. PA = polyamide (nylon-6), PASW = polyamide with silica (10 – 30 nm) in water media.

Wt% silica	Friction coefficient	Wear rate [mm ³ /Nm]
0	0.45	5.29×10^{-5}
2	0.20	2.0×10^{-7}
14	0.40	2.81×10^{-5}

Table I. Wear rate and coefficients of friction of PA6 (C) nanocomposites .
Velocity = 0.1 m/s Load=1N, Distance of sliding 10 km.

pictures have also shown the presence of voids in the films. However, if the resulting material is dense, Gardnes impact tests (falling ball impact) could be useful to do the measurements on these films.

The elastic modulus for composites with different filler percentages as tested with an extensometer is shown in Fig. 3. Already with 1 wt.-% silica addition, an increase in E-modulus could be observed; an E-modulus increase for 3 and 5 wt.-% loadings was sustained. Data points represent the average value after four tests for each sample.

Tribology

Table I gives the coefficient of friction and wear rate for PA-6 and its composites while sliding occurred against the steel counterface. The coefficient of friction of 2wt% of SiO₂ filled composite is lower than that of unfilled PA6. For addition of 14wt% of SiO₂, the coefficient of friction value was slightly lower than that of unfilled PA6 after few kilometres of wear track. The filler thus contributed to the reduction in wear rate of PA6 where 2wt% of silica were more effective in reducing the wear rate and was more effective in reducing the coefficient of friction as well.

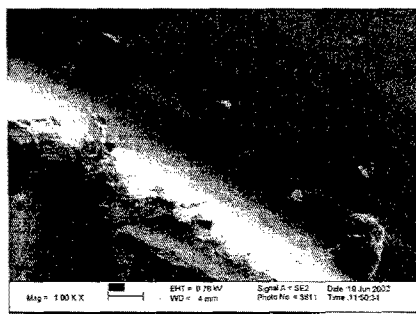


Figure 4. Wear track of 2wt%-silica/PA-6 nanocomposite.

CONCLUSIONS

The synthesis method described can be generally applied to all classes of polyamide-based composites that are susceptible to solvent dissolution. Inorganic filler material can be readily incorporated into the polymer matrix resulting in a hybrid nanocomposite with unprecedented control in particle size, mono-dispersity and homogeneity. An increase in E-modulus as a function of filler percentage added (0-5 wt.-%), a small decrease in yield strength (improvement in impact toughness) and a strain-at-break of >0.5 were obtained.

Furthermore, the addition of nano-silica to the PA-6 led to a lowering of the coefficient of friction and the wear resistance was improved. The minimum wear rate between the samples was obtained with 2wt% of filler addition.

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Fracture and Mechanical Properties II